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 T CHARGE-TRANSFER STATES IN ORGANIC SYSTEMS [REDACTED]  
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BY

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FACILITY FORM 602

N66 29362

(ACCESSION NUMBER)

8

(PAGES)

(NASA CR OR TMX OR AD NUMBER)

(THRU)

(CODE)

06

(CATEGORY)

GPO PRICE \$ \_\_\_\_\_

CFSTI PRICE(S) \$ \_\_\_\_\_

Hard copy (HC) 1.00Microfiche (MF) .50

ff 653 July 65

Translation of: "Sostoyaniya s perenosom zaryada v organicheskikh sistemakh."  
 Doklady Akademii Nauk SSSR, Vol. 144, No. 4, pp. 813-816, 1962.

→ NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
 WASHINGTON, D.C.

APR 1964

8p ref

NASA TT F-8848

→ vme.

Transl. into ENGLISH  
 from Dokl. Akad.  
 Nauk SSSR (Moscow)  
 Vol. 144, no. 4,  
 1962, pp. 813-816

## CHARGE-TRANSFER STATES IN ORGANIC SYSTEMS

V. A. Benderskiy and L. A. Blyumenfel'd

(Presented by Academician V. N. Kondrat'yev, January 8, 1962)

Organic polymers with conjugate bonds exhibit narrow (4-8 Oe), /813  
unique electronic paramagnetic resonance (EPR) signals of Lorentz  
shape with a g factor close to the pure spin value, the intensity of  
the signals varying regularly with the length of the conjugated sys-  
tem and remaining the same upon dissolving [1-4]. The number of un-

paired electrons N is  $10^{-5}$  to  $10^{-1}$  times the number of macromolecules  
and practically independent of the temperature.

A similar effect is found in the crystals of low-molecular com-  
pounds with conjugate bonds (polyacene hydrocarbons, their derivatives,  
dyes of various classes), but with this difference: the absorption  
disappears, reversibly, upon dissolving, and its intensity depends on  
the method of crystallization [5-9]. For these compounds, N is equal


to  $2 \cdot 10^{-4}$  to  $10^{-2}$  times the number of molecules and is likewise inde-  
pendent of the temperature. Two-component donor-acceptor crystals,  
one of the components of which has a low ionization potential I and  
the other a positive electron affinity A, possess the same magnetic

properties. N comprises  $4 \cdot 10^{-3}$  to 0.8 of the number of pairs and in-  
creases symbatically with decrease in  $I - A$  [10, 11]. Nevertheless,  
in all cases N remains independent of the temperature to 4°K.

Systems of all three types possess enhanced electrical conduc-  
tivity, governed by an exponential law [3, 12, 14]. In the case of  
single-component crystals, the activation energies for dark conduction  
 $\epsilon$  coincide with the photoconductivity threshold  $\epsilon_{ph}$  and the singlet-  
singlet transition energy [15]:

$$\epsilon = \epsilon_{ph} = \epsilon_0. \quad (1)$$

The study of photoconductivity reveals that the photocurrent  
is not a primary current, but is due to the thermal activation of  
carriers brought by the light to local levels [16, 23]. There is no  
direct relationship between the carrier density and the number of un-



paired electrons. In particular, there are mixed crystals with the same concentration of unpaired electrons but electrical conductivities differing by 6 orders of magnitude [14].

On the basis of these facts, we may state that the appearance of both unpaired electrons and current carriers in the compounds in question is due to local states\*. A typical property of systems with conjugate bonds may be seen in the low values of  $I - A$  and the high electron polarizability values; the spectrum of polar excited states (charge-transfer states) must be depressed below that typical of ordinary organic compounds. Some indication of the need to take polar excited states into account in the study of the magnetic and electrical properties of molecular systems of this type may be found in the literature [17]. In this paper, the opinion is advanced that the local states responsible for the electrical and magnetic properties of compounds of these three types are states involving charge transfer either between molecules or between discrete segments of conjugation in the molecule. This hypothesis provides a basis for an explanation of the formation of carriers in terms of a dissociation of complexes with charge transfer, as first suggested by Lyons [18].

/814

Let us now attempt to throw some light on the conditions governing the formation of local charge-transfer states in crystals and their concentration. To do this, let us consider the potential curves for the formation of a complex of two molecules in the neutral and polar states (Fig. 1). Since the dispersion interaction for a system of two ions is at least not less than that for neutral molecules, and, further, since a strong coulomb interaction takes place between the ions, the equilibrium distance between components in the formation of charge-transfer complexes must be less than that between neutral molecules:

$$R_O^i < R^0. \quad (2)$$

Relation (2) was recently confirmed experimentally [19]. The difference in the energies of the neutral and polar states is

$$\epsilon_i^0 = I - A - W(R_O^i), \quad (3)$$

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\*In order to account for the magnetic properties, we would have to assume that molecular interaction in sufficiently long conjugated chains results in partial mixing of the ground and lower excited magnetic states. However, an energy level calculation, carried out by D. A. Popov (in completion of his thesis requirements, Moscow State University, 1961), showed that this mechanism is inoperative for any length of the conjugated system.

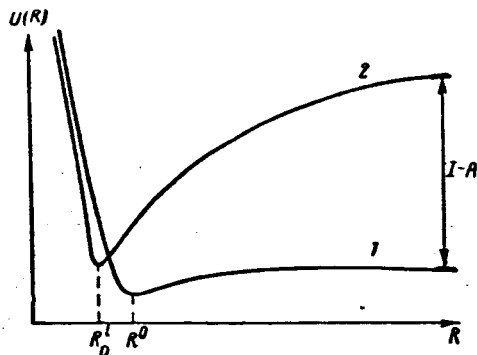


Fig. 1. Potential curves for a neutral pair (1) and a charge-transfer complex (2).

where  $W(R_1^0)$  is the coulomb interaction energy in the polar state.

Relation (3) also holds in the case of single-component crystals [17]. In solution, the difference between the energies of the ground state and the polar state is:

$$\epsilon_i^S = I - A - W(R_0^1) - W_S, \quad (4)$$

where  $W_S$  is the solvation energy of the ion pair formed. According to available data [20], the concentration of the complexes,  $n$ , is related to the pair concentration in the solution,  $N_0$ , as follows:

$$\frac{n^2}{N_0 - n} = N_0 e^{-\epsilon_i^S/kT}. \quad (5)$$

At the growth boundary,  $N_0$  attains a maximum, since the number of polar states appearing in the crystal during its formation will be higher than in solution. In accord with inequality (2), the appearance of polar states will lead to a local deformation of the crystal, and

$$\epsilon_0 (R_0^i) > \epsilon_i (R_0^i). \quad (6)$$

Consequently, the local state of the charge-transfer complex in the crystal will be a growth dislocation in which the molecules will be spaced at distances shorter than the equilibrium distances for a neutral crystal. A similar mechanism is, of course, in force when other methods are used to obtain the solid phase. Because of condition (6), the transition from polar to neutral state is impossible without a reordering of a substantial portion of the crystal. The concentration of local charge-transfer complexes will be independent of the temperature and is determined by the ionization potentials and the electron affinity, as one might expect from (4) and (5). Experimental verification of this model may be had by studying the variations in the concentration of polar states when the crystals are obtained from solvents with different dielectric constants at different temperatures.

Now, in proceeding to consider the electrical conductivity of the molecular crystals, we have to find the energy of dissociation of a local charge-transfer state with formation of a central ion, localized at the defect, and a free carrier. This problem reduces to determining the energy of polarization of the crystal due to the charge-transfer complex and two infinitely remote molecular ions. The problem was solved by the methods of quantum field theory. The motion of a conduction electron in a molecular crystal was found to be accompanied by an electron polarization wave following adiabatically behind the electron. This in turn results in a lowering of the intrinsic energy of the conduction electron. The energies of polarization of a crystal by negative and positive molecular ions are approximately the same and equal to

/815

$$E = - \frac{D}{v_0} K_{nn} \sum_i \frac{f_i}{\epsilon_i^2}, \quad (7)$$

where  $D$  is a numerical coefficient determined by the crystal geometry;  $v_0$  is the volume corresponding to a single molecule in the crystal;  $K_{nn}$  is the coulomb interaction integral of two electrons at the uppermost filled molecular orbital;  $f_i$ ,  $\epsilon_i$  are the oscillator strengths and energies of the excited states. Clearly, from (7), as the energy of the excited states declines, the polarization energy increases in accordance with a square law.

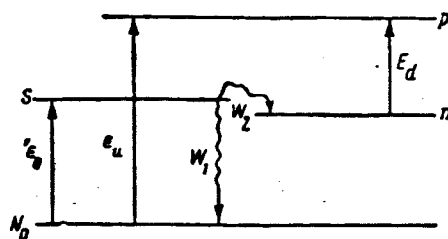


Fig. 2. Energy level scheme of model of an organic semiconductor.

p -- conduction band; n -- local level due to charge-transfer complex; S -- singlet exciton band.

The results of numerical calculations of the polarization energy  $E$  and dissociation energy  $E_d$  of the polar states in the crystals of aromatic hydrocarbons are:

TABLE 1

	$E$ , ev	$E_d$ , ev		$E$ , ev	$E_d$ , ev
Naphthalene	1.08	1.47	Naphthacene	1.76	0.78
Anthracene	1.39	1.08	Pentacene	1.95	0.48

Even in the case of comparatively simple systems, the polarization energies turn out to be rather high. For anthracene the experimental value of the polarization energy, equal to the difference between the ionization potentials in the gas phase and in the crystal, is known to be  $1.59 \pm 0.25$  ev [18], which is close to the theoretically predicted value. It has been shown that the dissociation of a charge-transfer complex requires an energy consumption

$$E_d = - \left( 1 - \frac{2D}{v_0} \sum_i \frac{f_i}{\epsilon_i} \right) W(R_0^i). \quad (8)$$

For numerical values of  $E_d$ , see the table above.

The dissociation energies fall off rather rapidly as the geometric dimensions of the molecules and the polarization energy increase.

In connection with the proposed model of local centers, there arises the additional possibility of charge carriers appearing in the molecular crystals. This mechanism is based on the dissociation of charge-transfer complexes at the expense of exciton energy. It was found that the probability of the process of transfer of the energy of an exciton to a local charge-transfer center is greater than the probability of spontaneous emission of an exciton quantum, when the

concentration of local states exceeds  $10^{16} \text{ cm}^{-3}$ . Processes of this type are well known in inorganic semiconductors [21, 22].

The energy level scheme of the proposed model is shown in Fig. 2. The photoconduction energy will coincide with the singlet-singlet transition energy. The steady-state carrier density  $p$  will also be dependent on the equilibrium concentration of excitons as given by

/816

$$p = N_0 e^{-\epsilon_u/2kT} + n e^{-E_d/2kT} + \gamma \frac{N_0}{(1 + W_1/W_2)} e^{-\epsilon_0/2kT}, \quad (9)$$

where  $W_1$  and  $W_2$  are, respectively, the probabilities of the deactivation and exciton decay processes, and  $\gamma \approx 1$ . When the conduction band lies above the lower singlet level, and the concentrations of charge-transfer complexes are comparatively low:

$$\epsilon_u > \epsilon_0, \quad n e^{-E_d/2kT} < N_0 e^{-\epsilon_0/2kT} \quad (10)$$

the carrier density will be determined by the energy of the singlet-singlet transition. When the conduction band lies below the excited singlet level, the main source of charge carriers will be excitation directly into the conduction band, which is described by the first term in (9). At high charge-transfer complex concentrations, the activation energy of electrical conduction will coincide with the dissociation energy of polar states, in accordance with formulas (8) and (9).

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